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Synthesis of Poly(propene-*g*-styrene) Graft Copolymers by Metallocene Catalyzed Copolymerization of Propene with Allyl-Terminated Polystyrene Macromonomer Obtained via Quasiliving Atom Transfer Radical Polymerization and the Effect of the Grafts on Blending Polypropene with Polystyrene

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ABSTRACT: Allyl-terminated polystyrenes (PS macromonomers) were synthesized by quasiliving atom transfer radical polymerization (ATRP) of styrene followed by carbocationic chain end transformation with allyltrimethylsilane in the presence of titanium tetrachloride. Systematic investigations were carried out on metallocene/MAO-catalyzed copolymerization of PS macromonomers with propene by varying the molecular weight of the macromonomer, the type of catalyst, the polymerization temperature, and the propene pressure. The resulting poly(propene-*g*-styrene) (PP-*g*-PS) graft copolymers were analyzed by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. Macromonomer incorporation, molecular weight, tacticity, and crystallinity of the resulting PP-*g*-PS copolymers were greatly influenced by the investigated parameters. The macromonomer incorporation depends mostly on the polymerization temperature. The highest comonomer incorporation (10.8 wt %) was achieved at the highest polymerization temperature, but at the same time the molecular weight decreases strongly with increasing polymerization temperature leading to graft copolymers with relatively low molecular weights. For the first time, the effect of well-defined PP-*g*-PS grafts was investigated on blending incompatible polypropylene with polystyrene. Surprisingly, it was found that PP-*g*-PS graft copolymers with short PS side chains show a better compatibilization efficiency than those with long PS chains at comparable composition as scanning electron microscopic investigations on the morphology of blends indicate.

Introduction

For compatibilization of immiscible polymer blends typically block or graft copolymers are used. To act as compatibilizer, some of the structural units must be miscible with one blend component, the other with the other blend component. Most widely studied are AB or ABA block copolymers as compatibilizers; however, in practice, mainly graft copolymers are used.

Polypropene (PP) and polystyrene (PS) belong to commodity polymers produced in large amounts with low costs. However, these homopolymers are immiscible, and their blends have poor mechanical properties. Thus, if someone wants to use PP/PS blends, the mechanical properties of the blends should be improved by the addition of compatibilizing agents. The ideal chemical structure for a graft copolymer as compatibilizer for PP/PS blends would be poly(propene-*g*-styrene) (PP-*g*-PS) graft copolymers composed of a PP main chain grafted with PS side chains. The preparation of these graft copolymers are commonly carried out by polymerization of styrene onto the PP backbone.[1,2] This "grafting from" method based on free radical polymerization initiated by functionalized PP or irradiation has the disadvantage of poor controllability. The limited ability to adjust the content of grafted units, the length, and the distribution of the side chains in the resulting graft copolymers do not allow one to study the influence of these parameters on the compatibilization efficiency of PP-*g*-PS.

However, these polymer architectures, i.e., PP-*g*-PS graft copolymers, can also be prepared by another approach, the macromonomer technique. This method involves the metallocene-catalyzed copolymerization of an olefin with a macromonomer, which is composed of a chain with defined length and a polymerizable terminal group. Thus, copolymerization of propene with PS macromonomers may allow the synthesis of well-defined graft structures with controlled side chain length. By variation of the macromonomer molecular weight and the copolymerization conditions, the number and length of side chains and the length of backbone may be adjusted. Consequently, a variety of PP-*g*-PS copolymers with well-defined architecture will be accessible by the macromonomer technique that makes systematic studies on their compatibilizing efficiency possible.

Arnold et al. demonstrated that allyl-terminated[3] (M_n = 4000 g/mol) or norbornenyl-terminated[4] (M_n = 700−18 000 g/mol) PS macromonomers can be copolymerized with propene by metallocene catalysis. The PS macromonomers were synthesized by anionic polymerization. Several anionically polymerized PS macromonomers were also tested in metallocene-catalyzed ethene

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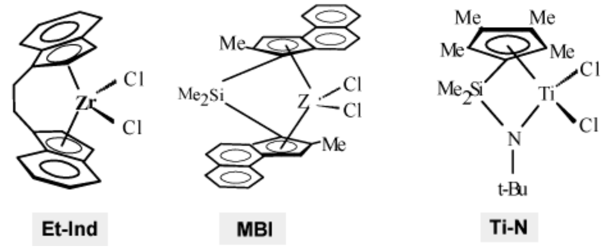
Scheme 1. Structure of Applied Metallocene Catalysts



copolymerization.[5] However, these studies do not report on either the effect substantial parameters, such as molecular weight of the macromonomer, type of metallocene catalyst, temperature, propene (or ethene) pressure, on the copolymerization behavior, the composition, and molecular weight of the resulting grafts, or on the blending efficiency of PP-*g*-PS graft copolymers in polypropylene/polystyrene blends.

Allyl-terminated PS macromonomers can be prepared also by quasiliving[6] atom transfer radical polymerization (ATRP) and subsequent chain end modification.[7] Alternatively, unreactive vinyl compounds, as one example demonstrates,[8] can be used for initiating ATRP to form a macromonomer. Compared to the anionic polymerization the ATRP technique[9] is less sensitive to impurities and a larger number of monomers can be polymerized by this method. Thus, the combination of ATRP with metallocene-based copolymerization is a favorable way for the synthesis of polyolefin graft copolymers with defined structure.

In this paper, a detailed study on the synthesis of PP-*g*-PS copolymers by the combination of ATRP and metallocene-based propene polymerization is reported. Copolymers of propene and polystyrene macromonomers of varied chain length were synthesized using different metallocene/methylaluminoxane (MAO) catalyst systems. The aim was to find a correlation between the synthesis conditions and the copolymer structure. Furthermore, the copolymers were tested as compatibilizer in blends of PP and PS. For the first time, a correlation between the structure of the PP-*g*-PS graft copolymer compatibilizers and the resulting morphology of melt-mixed PP/PS blends was also investigated.

Experimental Section

Chemicals. Styrene (Aldrich) was distilled under reduced pressure at room temperature. Dichloromethane (Chemolab, Hungary) was dried by refluxing over calcium hydride and was distilled under nitrogen atmosphere. Toluene (Fluka, p.a.) was dried by refluxing over Na/K alloy and finally distilled under argon atmosphere, and 2.8 grade propene was purchased from Riessner-Gase. It was purified by passing through 3 Å molecular sieves followed by R3-11 copper oxide catalysts (BASF). Methylaluminoxane (MAO) solution obtained from Witco was crystallized as white powder by distilling off the solvent (toluene) under vacuum. rac-Et[Ind)]$_2$ZrCl$_2$ (Et−Ind) (Witco), rac-Me$_2$Si[2-Me-4,5-BenzInd]$_2$ZrCl$_2$ (MBI) (BASF), and Me$_2$Si(t-BAMe$_4$Cp)TiCl$_2$ (Ti−N) (Witco) were used as received (Scheme 1).

Toluene for macromonomer preparation, methanol, tetrahydrofuran, and hexane (all from Chemolab), (1-chloroethyl)benzene (Acros), (1-bromoethyl)benzene, 2,2′-bipyridine (bpy), copper(I) chloride, copper(I) bromide, titanium tetrachloride, and neutral aluminum oxide (all from Aldrich), and allyltrimethylsilane (ATMS) (Fluka) were used as received.

Scheme 2. Synthesis of PS Macromonomers via Quasiliving Atom Transfer Radical Polymerization Followed by Carbocationic Chain End Modification

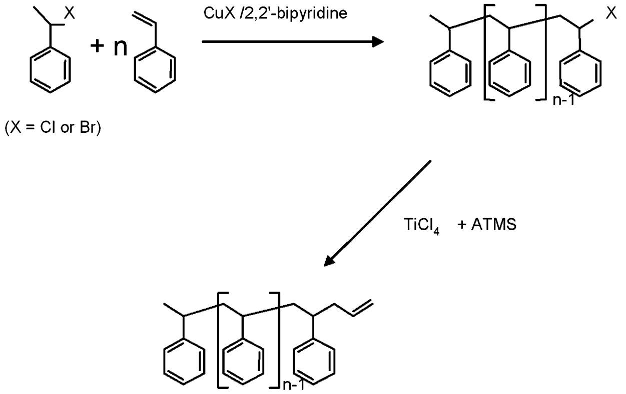


Table 1. Synthesis Conditions and Molecular Weights of PS Macromonomers

macromonomer	sample	polymerzn time, h	initiator[a]	M_n, g/mol	M_w/M_n
1	PS(18 000)	24	PhEtCl	18 300	1.57
2	PS(11 000)	16	PhEtBr	10 700	1.17
3	PS(2000)	3	PhEtBr	2040	1.29
4	PS(1300)	3	PhEtBr	1260	1.21

[a] PhEtBr = (1-bromoethyl)benzene. PhEtCl = (1-chloroethyl)benzene.

Synthesis of Macromonomers. Polystyrenes with 2-chloro-2-phenylethyl or 2-bromo-2-phenylethyl chain end were synthesized by quasiliving atom transfer radical polymerization of styrene in bulk (Scheme 2). The initiator was (1-chloroethyl)benzene or (1-bromoethyl)benzene and the catalyst was copper(I) chloride or copper(I) bromide complexed with bpy. The molar ratio of initiator:CuCl (or CuBr):bpy was 1:1:2.5. The initiator:styrene ratio was calculated from the desired molecular weight of the macromonomer. After deoxygenating with three freeze/pump/thaw cycles the polymerization was carried out at 130 and 110 °C for different periods depending on the initiator/monomer ratio. The resulting polymers were dissolved in THF, and the solutions were passed through a chromatography column filled with neutral aluminum oxide. The polymers were precipitated into methanol, filtered off, and dried in a vacuum oven at 40 °C.

The halogen-terminated polymers were added into round-bottom flasks which were sealed with a septum and purged with argon. After the polymers were dissolved in dichloromethane, 3 equiv of titanium tetrachloride and 3 equiv of ATMS were added to the stirred solutions. Then, 20 min later the flasks were opened and some methanol was carefully added in order to deactivate the titanium tetrachloride. An equal volume of toluene was added, the solid part (titanium oxide) was filtered off, and subsequently dichloromethane and methanol were evaporated off. The polymer solutions were passed through a chromatography column filled with neutral aluminum oxide and were precipitated into methanol. After filtration and drying, the polymers were dissolved again in dichloromethane and precipitated into cold hexane. Finally, they were filtered off and dried to constant weight in a vacuum oven at 70 °C.

Homo- and Copolymerization. Propene polymerizations were carried out in 200 mL toluene in a 1 l glass autoclave (Büchi) equipped with a stirrer, manometer, thermocouple, heating, and cooling units. The propene consumption was monitored by a pressflow-gas controller (Büchi). The temperature, speed of stirrer, pressure, instantaneous gas flow, and total gas consumption were monitored and recorded online. The stirring speed was kept constant at 800 rpm. The polymerization temperature was varied from 30 to 70 °C, and the total pressure was set in the range 1−3 bar (Table 2).

The reactor was first charged with the cocatalyst MAO, the macromonomer, and toluene. Then it was loaded with propene three times to 2 bar overpressure and expanded to atmospheric pressure while stirring. The solution was saturated with

Table 2. Synthesis Conditions (Macromonomer, Metallocene Catalyst, Polymerization Temperature (T_{pol}), Total Pressure (p_{total}), and Macromonomer Conversion (Convn)) and Properties of Resulting Graft Copolymers (Comonomer Content, Number-Average Molecular Weight (M_n), Polydispersity (M_w/M_n), Isotacticity, Number of Side Chains per Molecule (n_{PS}), Melting Temperature (T_m), and Degree of Crystallinity (α_{PP})) Obtained by Copolymerization of Propene with PS Macromonomers

sample	macromonomer	metallocene	T_{pol}, °C	p_{total}, bar	convn, %	comonomer content, wt %	M_n, g/mol	M_w/M_n	isotacticity, % *mmmm*	n_{PS}	T_m, °C	α_{PP}, %
PP−PS-9	PS(18 000)	MBI	50	1.5	30.2	6.7	89 400	1.9	54	0.33	151	24
PP−PS-17	PS(11 000)	MBI	50	1.5	31.6	7.0	80 300	2.0	54	0.56	150	24
PP−PS-10	PS(2000)	MBI	50	1.5	40.2	8.7	54 000	2.2	36	2.1	148	15
PP−PS-14	PS(18 000)	MBI	30	1.5	8.9	2.4	285 000	1.9	91	0.37	158	40
PP−PS-15	PS(18 000)	MBI	70	1.5	43.1	10.8	33 200	2.1	61	0.20	144	23
PP−PS-7	PS(18 000)	MBI	50	1	31.4	7.4	78 900[b]	1.8	61	0.33	150	28
PP−PS-6	PS(18 000)	MBI	50	2	21.9	4.9	*c*		41	0.22	150	20
PP−PS-11	PS(18 000)	Ti−N	50	1.5	20.8	7.4	194 900	1.7	2	0.8	*a*	0
PP−PS-19	PS(11 000)	Ti−N	50	1.5	17.1	9.1	97 200	2.0	2	0.88	*a*	0
PP−PS-20	PS(1300)	Ti−N	50	1.5	15.8	8.3	66 700	2.1	2	5.6	*a*	0
PP−PS-16	PS(18 000)	Et−Ind	50	1.5	27.9	6.2	10 600	2.1	83	0.04	127	25

[a] No melting peak. [b] M_w: 145 500. [c] M_w: 183 300.

Table 3. Synthesis Conditions (Metallocene and Polymerization Temperature (T_{pol})) and Properties (Number-Average Molecular Weight (M_n), Polydispersity (M_w/M_n), Isotacticity, Melting Temperature (T_m), and Degree of Crystallinity (α)) of PP Homopolymers Obtained under Different Polymerization Conditions

sample	metallocene	T_{pol}, °C	p_{total}, bar	M_n, g/mol	M_w/M_n	isotacticity, % *mmmm*	T_m, °C	α, %
PP-31	MBI	30	3	197 000	3.9	97	152	48
PP-53	MBI	50	3	110 300	2.7	67	151	36
PP-54	MBI	70	3	34 400	2.7	53	145	28
PP-42[a]	Et−Ind	30	3	20 500	2.0	89	139	43

[a] For blend preparation.

propene at the desired total pressure thereafter. Finally, the polymerization was initiated by injecting the catalyst solution into the reactor. The catalysts were either Et−Ind, MBI, or Ti−N (see Scheme 1). For the copolymerization, the Al/Zr molar ratio was 4000 or 8000, and the catalyst concentration was 8 × 10^{-6} mol/L for catalysts MBI and Et−Ind or 1.6 × 10^{-5} mol/L for Ti−N. PS macromonomers with molecular weights between M_n = 1260 and 18 300 g/mol were used, assigned as PS(18 000), PS(11 000), PS(2000), and PS(1300) (see Table 1). The macromonomer concentration in the feed was 25 g/L. For homopolymerizations, the catalyst concentration was 8 × 10^{-6} mol/L and the Al/Zr molar ratio was 4000.

After consumption of 0.5 mol of propene the polymerization was terminated by injecting a small amount of ethanol. The reaction solution of the graft copolymer was precipitated into a mixture of ethanol, water, and some hydrochloric acid. The resulting copolymer was filtered, washed with water and ethanol, and dried overnight in a vacuum oven at 70 °C. To remove the nonincorporated PS macromonomer the filter cake was dissolved in hot xylene (20 g/dm^3), and then the solution was dripped into acetone and the copolymer was precipitated. After 4 h of stirring, the precipitate was filtered off and the graft copolymer was washed with acetone and dried in a vacuum oven at 70 °C for 1 day. The homopolymers were precipitated as described earlier.[10,11]

Preparation of Blends. For the preparation of PP/PS blends, a co-rotating twin-screw Micro-Compounder (Daca) with an overall volume of 4.5 mL was used. The composition of PP/PS blends was always 2/1 and different amounts of compatibilizer were added. The mixing conditions were as follows: T = 200 °C, 100 rpm, and 5 min mixing time. The PP used was synthesized by metallocene polymerization, indicated as PP-42 in Table 3 (M_n = 20 500 g/mol, M_w/M_n = 2.0) and the used PS was synthesized by the TEMPO method[12] (M_n = 21 600 g/mol, M_w/M_n = 1.6).

Polymer Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz (^{1}H) or 125.74 MHz (^{13}C). The samples were measured at 120 °C in $C_2D_2Cl_4$ which also was used as reference and lock.

Molecular weights of PP and PP-*g*-PS were determined by using high-temperature size exclusion chromatography (Polymer Laboratories 210 GPC) operated at 135 °C. The GPC apparatus had a column set with four columns (PL gel 20 μm Mixed-A). The mobile phase was 1,2,4-trichlorobenzene with a flow rate of 1.0 mL/min. The calibration was carried out by using PP with known molecular weight and distribution.

Molecular weights of PS macromonomers were determined by gel permeation chromatography with a Waters/Millipore liquid chromatograph equipped with a Waters 515 pump, Ultrastyragel columns of pore sizes 1 × 10^5, 1 × 10^4, 1 × 10^3, and 500 Å, and a Viscotek parallel differential refractometer/viscometer detector. Measurements were carried out at room temperature. Tetrahydrofuran was used as the mobile phase with a flow rate of 1.5 mL/min. Calibration was made with narrow MWD polystyrene standards.

The melting temperature and the heat of fusion were measured with a DSC 7 (Perkin-Elmer) equipment. Samples were subjected to a cycle of first heating, cooling and second heating with a scan rate of 20 K/min over a temperature range from −60 to +180 °C. Since the processing conditions can influence the thermal behavior of the sample in the first heating, only the second heating was evaluated. The melting temperature T_m was set as the temperature at the maximum of the melting peak. The degree of crystallinity of the PP part, α_{PP}, was estimated by integrating the heat flow between 90 and 165 °C using the real concentration of PP in the sample and the value for the heat of fusion of 100% crystalline PP, ΔH_0 = 208 J/g.[13]

The morphology of the samples was observed by scanning electron microscopy (SEM) using a DSM 982 Gemini (Zeiss Oberkochen) equipment at an acceleration voltage of 5 kV. The samples were cut and from the resulting smooth surface the PS phase was etched at room temperature with THF for 4 h. Before the measurements the samples were sputtered with gold.

Results and Discussion

Synthesis and Structure of PP-*g*-PS. For studying the influence of structural parameters of poly(propene-*g*-styrene) (PP-*g*-PS) graft copolymers on their compatibilizing efficiency it is necessary to have well-defined graft copolymers with large variation in the microstructure of the PP backbone (M_n, M_w/M_n, and tacticity) and in the graft copolymer structure (comonomer content and molecular weight of the PS macromonomer). To achieve these goals, i.e., to synthesize PP-*g*-PS graft copolymers with a variety of structures and compositions, several allyl-terminated PS macromonomers were obtained by quasiliving atom transfer radical polymerization (ATRP) and subsequent quantitative chain end derivatization. Three different metallocene catalysts were also tested for the preparation of the target graft copolymers. According to our knowledge, such systematic investigations have not been carried out so far. Furthermore, this is the first study that reports on the application of olefin-terminated polystyrene macromonomer obtained via quasiliving ATRP and used for graft copolymer syntheses by metallocene-catalyzed copolymerizations.

The use of quasiliving ATRP for the preparation of PS macromonomers has several advantages compared to anionic polymerization applied in earlier studies.[3−5] Radical polymerizations are less sensitive to impurities (water, oxygen, etc.) and a larger variety of monomers are polymerizable thereby, while the resulting polymers have also narrow molecular weight distributions and high chain end functionalities. Thus, it is favorable to prepare the PS macromonomers by the more convenient ATRP and subsequent terminal modification[7] instead of anionic polymerization. The synthesis of allyl-terminated PS, which can be considered as a substituted propene macromonomer, is outlined in Scheme 2. In the first step, quasiliving ATRP of styrene led to halogen- (Cl- or Br-) terminated PS. After purification, this polymer was converted to allyl-ended PS by reacting it with ATMS in a reaction mimicking quasiliving carbocationic polymerization[14,15] by the addition of $TiCl_4$ as Lewis acid, but in the absence of any monomers. This reaction proceeds via the formation of polystyryl cation and $Ti_2Cl_9^-$. The carbocation addition to ATMS results in the allyl-terminated polymer.[16] As shown in Table 1, PS macromonomers were synthesized with molecular weights of 1260, 2040, 10 700, and 18 300 g/mol. According to the applied analysis by ^{1}H NMR spectroscopy, the conversion of the halogen chain ends to allyl groups were quantitative since no detectable signals were found in the spectra in the 4.3−4.6 ppm range characteristic for the methine protons adjacent to the terminal halogen atom.[7] Thus, the average functionality of the macromonomers can be considered as high as the functionality of the halogen-terminated precursor PS formed by ATRP[9] which has been reported to be near to one. The preparation conditions and some characteristics of the macromonomers are listed in Table 1.

Since the conversion of PS macromonomers during the copolymerization with propene was expected to be incomplete, a purification method to get pure graft copolymers free of noncopolymerized PS macromonomers was developed. Therefore, physical mixtures of PP and PS homopolymers with different molecular weights were made. Their solutions in hot xylene (130 °C) with different concentrations were dripped into cold acetone. After 4 h of stirring, the precipitate was filtered, washed with acetone, dried, and analyzed by ^{1}H NMR. When the initial concentrations of PP was 4 g/dm^3 and of PS was 16 g/dm^3 it was found that the detectable amount of PS in the filter cake was always lower than 0.5 wt %. The quantity of PS remained in the filter cake was dependent on the M_n of PP but even in the case of PP/PS mixture with M_n of PP of 200 000 g/mol and M_n of PS of 18 300 g/mol, respectively, this value was not exceeded. Since no higher molecular weight copolymers were expected, this purification procedure, i.e., the precipitation of a 20 g/dm^3 polymer solution from hot xylene into cold acetone, was applied for purification of all samples.

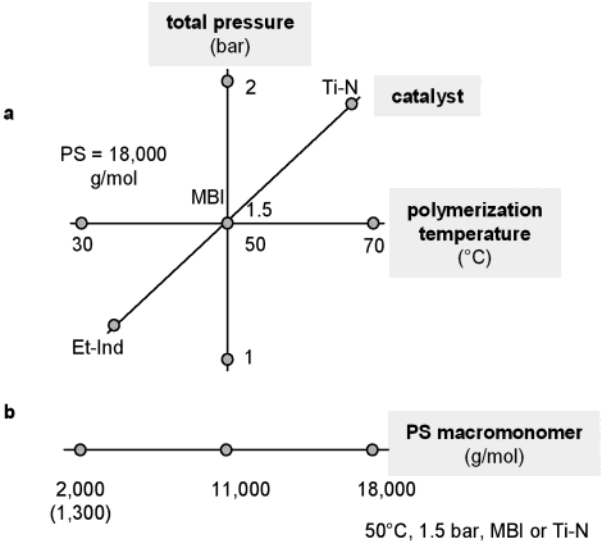


Figure 1. Variation of synthesis conditions for experiments with PS(18 000) (a) and for experiments with different macromonomer lengths (b).

A systematic investigation was carried out on the influence of the synthesis conditions on the structure of PP-*g*-PS. As presented in Figure 1 and Table 2, polymerization temperature, propene pressure (which correlates to the propene concentration), type of catalyst, and molecular weights of the PS macromonomers were varied to obtain copolymers with different properties. The resulting polymers were characterized by several techniques. Since a PP standard was used for the determination of the molecular weight averages of the copolymers the calculated values may be not absolutely correct due to the structural differences between homopolymers and graft copolymers, but the tendencies in the molecular weight change are well indicated. The incorporation of PS macromonomer into the PP chains was proven and quantified by ^{1}H NMR spectroscopy. As is shown in Figure 2, the characteristic aromatic proton signals of PS appear in the 6.5−7.3 ppm region indicating the formation of the targeted PP-*g*-PS graft copolymer. The conversion of PS macromonomer was calculated from its feed concentration and the copolymer yield and composition. The average number of side chains per molecule, n_{PS}, was determined from the graft copolymer composition and the molecular weights of the graft copolymers and the side chains. The microstructure of the PP backbone (tacticity) was determined from the methyl pentad region of the ^{13}C NMR spectra (Figure 3). The results are listed in Table 2.

The effect of polymerization temperature, T_{pol}, on the copolymerization behavior was investigated in copolymerizations with MBI as catalyst and with the macromonomer PS(18 000) at 1.5 bar of total pressure. Higher polymerization temperature reduces the solubility of propene, i.e., its concentration in the solution, on one hand. On the other hand, the propagation rate constants, the relative reactivity of propene vs macromonomer, and the rate constants of chain transfer and

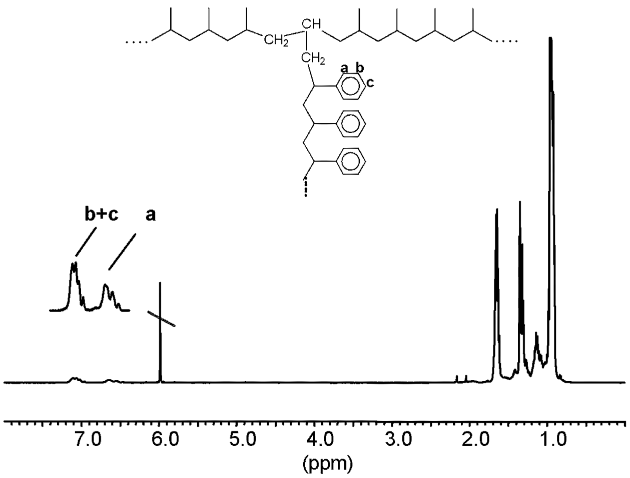


Figure 2. ^{1}H NMR spectrum of a PP-*g*-PS copolymer with isotactic backbone. T_{pol}: 50 °C. Total pressure: 1.5 bar, PS(18 000). Catalyst: MBI.

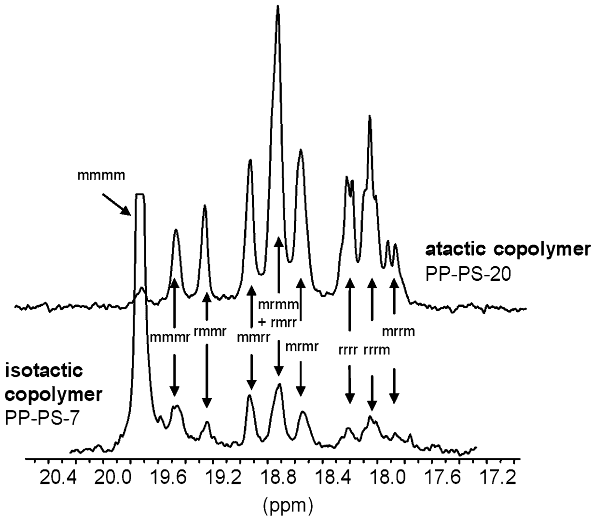


Figure 3. Methyl pentad region with stereosequence assignments from ^{13}C NMR spectra of copolymers with isotactic and atactic backbone. T_{pol}: 50 °C. Total pressure: 1.5 bar, PS(18 000).

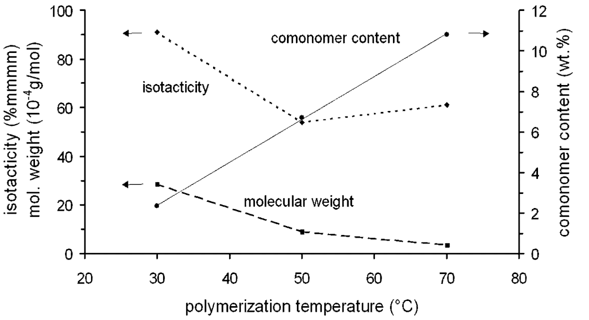


Figure 4. Correlation between copolymer structure and polymerization temperature. Total pressure: 1.5 bar, PS-(18 000). Catalyst: MBI.

termination are also influenced by T_{pol}. Figure 4 shows the effect of T_{pol} on the PS content, M_n, and backbone isotacticity of the copolymers. The PS content of copolymers strongly increases with increasing polymerization temperature. This tendency can be explained in part by the more favorable concentration ratio of PS macromonomer to propene. A change in the relative reactivity of propene vs macromonomer may also contribute

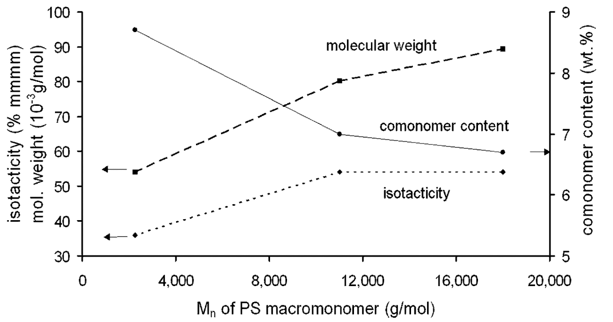


Figure 5. Correlation between copolymer structure and M_n of PS macromonomer. T_{pol}: 50 °C. Total pressure: 1.5 bar. Catalyst: MBI.

to the increased PS macromonomer incorporation. Similar to the homopolymerization of propene, the M_n of the resulting copolymers decreases with increasing T_{pol}. Comparing the adequate values in Table 2, it can be found that the opposite effects of increased PS incorporation and rather strongly decreased M_n of the copolymer results in only comparatively small decrease in n_{PS}. Apparently, the isotacticity decreases with enhanced polymerization temperature but no good correlation was found as in the case of homopolymerization (compare to Table 3). The expected reduced tacticity was not observed when T_{pol} was raised from 50 to 70 °C (Figure 4). This result indicates that the isotacticity is influenced by a rather complex interaction of several parameters which are not completely known yet.

The effect of propene pressure on PS content and M_w (with this series it was only possible to determine M_w for the sample PP−PS-6 with sufficient accuracy) of copolymers was studied using MBI as catalyst and the PS(18 000) macromonomer at $T_{pol} = 50$ °C. As the data indicate in Table 2, the PS incorporation is enhanced and the M_w of copolymer decreases with reduced propene pressure. These changes are caused by the lower concentration of propene in the solution. While the copolymer backbone becomes shorter and the PS content increases, the n_{PS} value remains almost unaffected as the result of these changes.

The longer PS side chains in the resulting graft copolymers are thought to lead to better compatibilization efficiency and better physical properties of PP/PS blends because of stronger interactions between PS chains of the homo- and copolymers.[17] Therefore, most PP-*g*-PS were synthesized by copolymerization of PS macromonomers with higher M_n in the course of our investigations. The influence of the molecular weight of PS macromonomer on the copolymer structure was also studied in experiments with MBI as catalyst at 1.5 bar at 50 °C (Figure 5). The hindered accessibility of the allyl groups in the longer PS chains was expected to cause lower apparent reactivity of PS macromonomers. Some decrease in PS content and moderate increase in M_n can be observed with increasing M_n of the PS macromonomer. The largest differences in the structure of these copolymers are in the values for n_{PS} (see Table 2). For the copolymers of propene with the macromonomer PS(18 000) n_{PS} was calculated as one side chain per three molecules, and with PS(11 000) as one side chain per two molecules. Better results were found by using the short chain macromonomers. The synthesized copolymers contain two side chains per molecule for PS(2000) or even five for PS(1300) when the system is catalyzed with Ti−N. These findings are

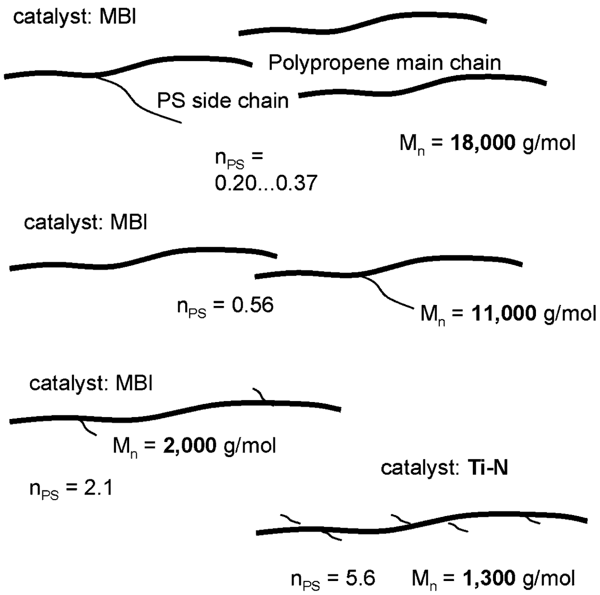


Figure 6. Schematic structure of the PP-*g*-PS copolymers prepared by copolymerization of propene with allyl-terminated PS having different M_n under similar conditions.

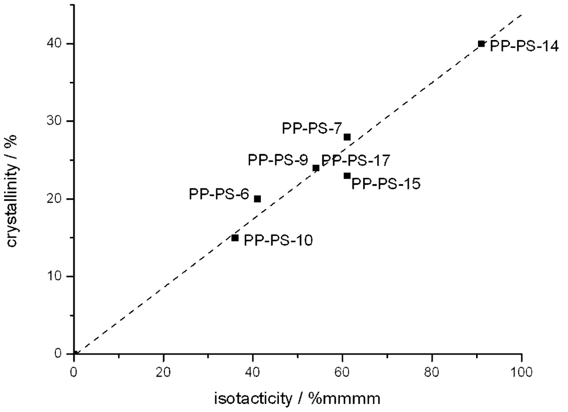


Figure 7. Dependence of crystallinity on tacticity. Catalyst: MBI.

illustrated in Figure 6. Because of the fact that chains with more than one side chain per molecule can also be synthesized we can conclude that the PS macromonomers do not terminate the growing PP chains.

It must be mentioned that the M_n of PS macromonomer is not the determining factor for yielding graft copolymers with so different n_{PS} values. In these experiments the molal concentration of PS macromonomer was kept constant (25 g/L) while the molar concentration highly depends on M_n of the macromonomer. With lower M_n the molar concentration, i.e., the molar ratio of PS macromonomer to propene, was more favorable, resulting in higher molar incorporation ratio and higher n_{PS}. To compare the reactivity of macromonomers, i.e., to determine the influence of chain length thereon, the conversion values can be used. The reactivity of PS(2000) is only about 1.33 times higher than that of PS(18 000). This means that the expected reduced accessibility of the allyl groups due to longer polymer chains has some influence on the reactivity, but does not modify it by order of magnitudes.

The effect of catalyst on the graft copolymer structure was investigated by copolymerizations of propene with PS(18 000) at 1.5 bar pressure at 50 °C. As expected, the catalyst has considerable influence on

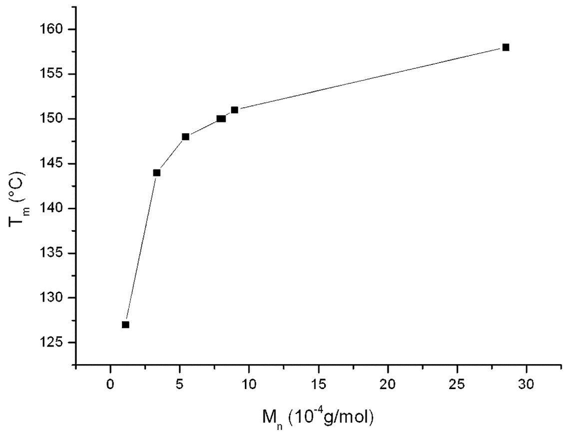


Figure 8. Melting temperature of copolymers determined from the second heating as a function of their molecular weight.

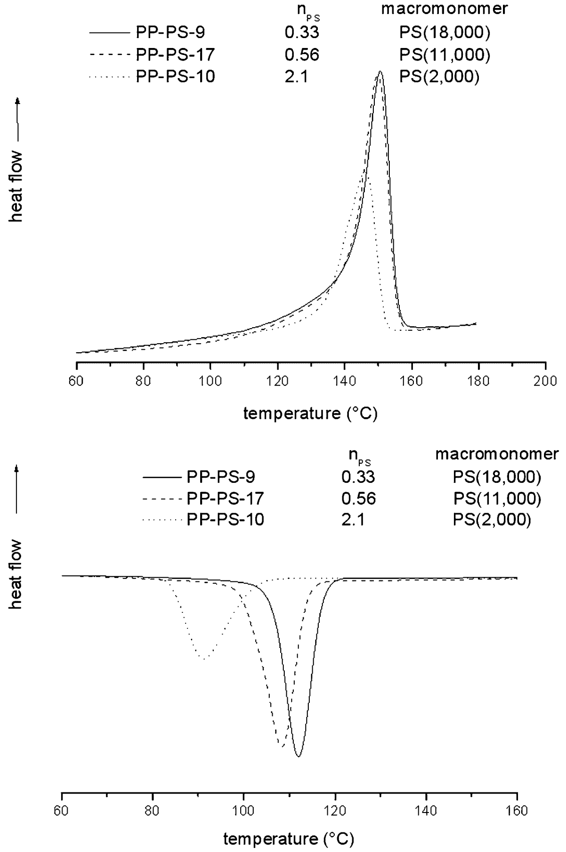


Figure 9. Melting and crystallization behavior dependence on the number of side chains per molecule. T_{pol}: 50 °C. Total pressure: 1.5 bar. Catalyst: MBI.

M_n and backbone tacticity of PP-*g*-PS graft copolymers. With MBI and Et−Ind isotactic and with Ti−N atactic copolymers were formed, although, as it was discussed above, the stereoregularity of isotactic copolymers decreases due to the pendant chains compared to PP homopolymer. The M_n of copolymers give the same tendency as it was observed in propene homopolymerizations since it is mainly determined by the rate ratio of chain propagation and chain termination.

Thermal Properties of PP-*g*-PS. As is known, the macromonomer content in a copolymer has significant influence on the melting and crystallization behavior (melting temperature T_m; onset temperature of the

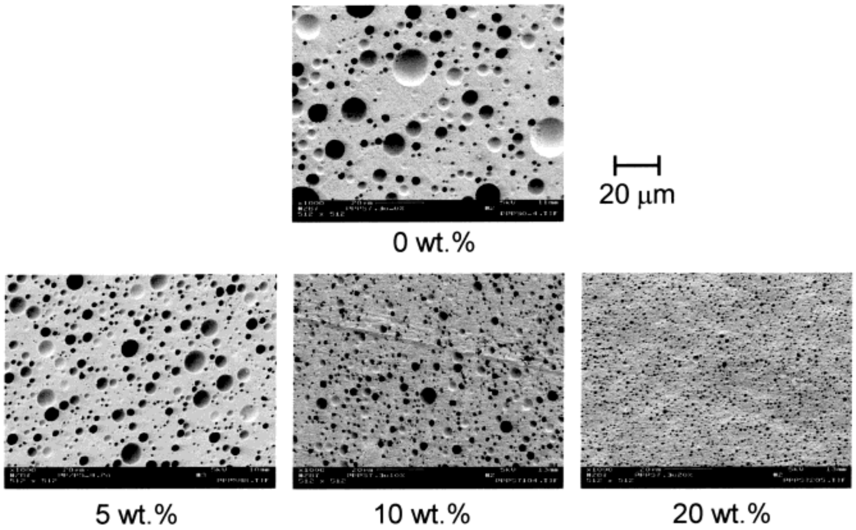
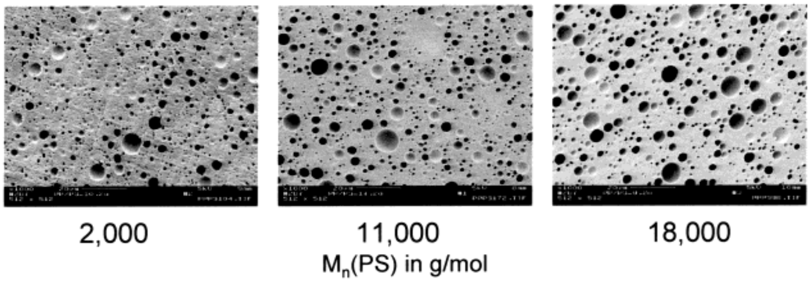


Figure 10. Influence of the compatibilizer content on the PP/PS morphology. Polymer blends PP/PS = 2/1 with varied isotactic PP−PS-7 copolymer content.

a: with isotactic copolymer, content of PS macromonomer: 6.7 ... 8.7 wt.%



b: with atactic copolymer, content of PS macromonomer: 7.3 ... 8.3 wt.%

Figure 11. Influence of the copolymer structure on the blend morphology. Polymer blends PP/PS = 2/1 with 5 wt % isotactic (a) or atactic (b) copolymer.

crystallization $T_{c,o}$, and crystallinity α_{PP}) of isotactic copolymers.[3] We also observed a drop in T_m and α_{PP} for the PP-*g*-PS graft copolymers compared to PP prepared at similar polymerization conditions (see Tables 2 and 3). However, this tendency is overlapped by further parameters.

At first we studied the influence of the isotacticity of the backbone on the melting and crystallization behavior for the copolymers produced with MBI catalyst. The isotacticity itself is a function of the process parameters, such as temperature, pressure, and M_n of the macromonomer, as shown in Figures 4 and 5. In Figure 7, the crystallinity α_{PP} is plotted against the isotacticity. A linear function was obtained, although other characteristic parameters like the comonomer content, the molecular weight, and the n_{PS} value also vary. This means that the isotacticity is dominant in regard to the crystallinity.

As shown in Figure 8, the melting temperatures of PP-*g*-PS graft copolymers directly depend on the molecular weights of the copolymers (Table 2). Such behavior is typical for homopolymers of propene as well in the investigated molecular weight region (Table 3). This dependence is also observed explicitly for samples prepared by the variation of the polymerization temperature, where the isotacticity does not follow the same tendency. The sample with the smallest M_n prepared with the Et−Ind catalyst also satisfies the expected dependence.

Finally, we discuss the crystallization behavior. Apparently, the number of side chains per molecule, n_{PS}, influences above all the crystallization kinetics. Both the extrapolated onset temperature of the crystallization ($T_{c,o}$) and the rate of crystallization characterized by the reciprocal value of the breadth of the crystallization peak show the lowest values for sample PP−PS-10 with the highest value of n_{PS} = 2.1 (Figure 9). However, a direct relation of the crystallization parameters to n_{PS} could not be found. This indicates that other parameters play also a vital role in the kinetics of the crystallization process.

PP-*g*-PS as Compatibilizer in PP/PS Blends. Of special interest was to investigate the influence of the structural parameters on the compatibilizing efficiency of PP-*g*-PS copolymers. Therefore, we studied the morphologies of melt mixed PP/PS blends with a composition of 2/1 without and with addition of different PP-*g*-PS graft copolymers. Under this condition PP always formed the matrix and PS the dispersed phase, which could easily be removed from cut surfaces by dissolution with THF. In SEM images, the original PS phase appears then as holes. The model blend system PP/PS is very incompatible and compatibilizing effects due to the copolymer addition should be clearly visible.

In a first series, different amounts (1−20 wt %) of PP−PS-7, a graft copolymer with isotactic backbone, rather high molecular weight, long PS side chains and an average grafting degree of 0.33 (Table 2), were added to the PP/PS blend to study the amount necessary for effective compatibilization. As is shown in Figure 10, the particle size in the blends strongly depends on the compatibilizer content but a significant reduction in the size of the dispersed PS phase is observed when at least 5 wt % of the copolymer were added. The finest dispersion is observed with the highest amount of compatibilizer added. The high amount of copolymer necessary to reach effective compatibilization in PP/PS blends can be explained by the relative low PS content in the PP-*g*-PS graft copolymer which hampers strong interactions to the PS phase. Thus, higher PS contents in the graft copolymers should be achieved for better compatibilization efficiency. Higher PS content can be gained by varying the parameters in the direction indicated by the copolymerization results presented in this study and/or by increasing the PS macromonomer feed during copolymerization.

In a second series, 5 wt % of PP-*g*-PS which differ in the molecular weight of the PS macromonomer, backbone tacticity, and n_{PS} at similar overall PS content were tested as compatibilizers. Opposite to our expectation the graft copolymers with the same PS content but shorter side chains show better effect in compatibilization than those with longer side chains (Figure 11). This surprising finding is probably caused by the low n_{PS} value (<1) of copolymers with long side chains (see Figure 6). These are mixtures of real graft copolymer and PP homopolymer chains which cannot act as compatibilizer. Therefore, the actual concentration of the PP-*g*-PS compatibilizer is lower than 5 wt % in these instances. The tacticity of the PP main chain does not influence significantly the compatibilization efficiency since the blend preparation occurs in the melt state. It seems that both the isotactic and the atactic copolymers reduce the interfacial tension as one main mechanism to reach fine dispersions during melt mixing.

Conclusions

The combination of quasiliving atom transfer radical polymerization (ATRP) of styrene, to obtain allyl-terminated PS macromonomers, with the metallocene-catalyzed copolymerization of these macromonomers with propene is a convenient way to synthesize poly(propene-*g*-styrene) graft copolymers. By adjustment of the reaction conditions high control of the microstructure of the polymer backbone and the structure of the resulting graft copolymers can be achieved. The thermal properties of these copolymers depend strongly on the isotacticity, number of grafts per chain, and the graft copolymer molecular weight.

For the first time, the influence of the PP-*g*-PS graft copolymer structure on the compatibilization efficiency for PP/PS blends was also investigated. It was found that the compatibilizing efficiency significantly depends on both the amount and the length of PS side chains attached to the PP backbone. Surprisingly, atactic copolymers show a similar efficiency like PP-*g*-PS with isotactic backbone. One limiting factor of the relatively small compatibilizing efficiency of PP-*g*-PS with long PS side chains seems to be the rather small PS content in these graft copolymers.

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